HYDROTREATMENT AND BIOLOGICAL TEST OF SRC-II COAL LIQUID

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Introduction

Distillate coal liquid from the SRC-II process has been hydrotreated at several levels of severity in a bench-scale continuous flow unit at the Bartlesville Energy Technology Center. The purpose was twofold with the immediate goal to survey process conditions with a commercially available catalyst to provide samples upgraded to varied degrees for detailed characterization analyses and investigation for biological activity. Long-range goals are to contribute to a data base to evaluate raw material sources, liquefaction or other production processes, characterization of feedstocks for further refining to transportation and other end-use fuels, selection of refining processes, and estimation of type and quality of end products expected from combinations of these steps.

The liquid feed and products have been screened for biological activity by the Ames test at Lovelace Biomedical and Environmental Research Institute, Albuquerque, New Mexico.

Experimental Materials and Procedures

The SRC-II liquid was obtained from the Pittsburg and Midway Coal Mining Co. The liquid was produced from Material Balance Run No. 77 SR-12 on coal from the Pittsburg seam from Consol's Blacksville No. 2 Mine in West Virginia. The middle (177-288° C) and heavy (288-454°C) distillates were blended to the same ratio as produced by the material balance run, e.g., 75.5 percent middle distillate and 24.5 percent heavy distillate. The feed contained 0.23 wt-pct sulfur, 1.06 wt-pct nitrogen and 3.29 wt-pct oxygen and boiled between 185 and 380° C (5-95 percent) by simulated distillation.

The bench-scale hydrogenation unit was designed for operation at up to 3,000 psig and 450° C, with once-through flow of hydrogen, down-flow of gas and liquid over a fixed-bed catalyst. Reactor temperature, pressure, and hydrogen flow and liquid level in the high-pressure product separator were controlled automatically. Liquid product was withdrawn periodically from a low-pressure separator, and the combined high- and low-pressure effluent gas was sampled for analysis.

The catalyst was 100 ml of American Cyanamid HDS-3A, a 1/16-inch diameter extrudate of nickel-molybdenum-alumina. It was diluted with inert, granular alpha-alumina to provide a bed depth of 18 inches in the middle section of a 0.96-inch ID vertical reactor with a 5/16-inch OD internal thermocouple well. The catalyst was progressively more dilute toward the top of the bed to minimize exothermic temperature effects, and end sections were packed with alpha-alumina to provide for preheat and cooling zones.

The catalyst was presulfided and operated for about 100 hours on a petroleum gas oil (200-500° C boiling range, 0.8 wt-pct sulfur) to check controls and provide some catalyst aging before exposure to the coal liquid.

Operating conditions selected as likely to maintain catalyst activity and provide the range of upgrading desired were 2,000 psig pressure, 325 to 400° C, and 0.5 to 1.0 LHSV (volume liquid feed/volume bulk catalyst/hour). Hydrogen flow was held constant at a rate corresponding to 10,000 SCF/bbl to 0.5 LHSV or 5,000 SCF/bbl at 1.0 LHSV. Variation in hydrogen flow rate in once-through operation has little effect at more than 5,000 SCF/bbl. Operation at each condition was for approximately 24 hours to allow 8-12 hours for equilibration plus time to accumulate about 750 ml of liquid product. Table 1 shows the sequence of reactor conditions and essential process results.

TABLE 1. Process conditions and results

	Liquid Product					Approx.	Catalyst	Liquid
Sample Period	Sp. gr., 60°/60°F	Hydrogen, wt-pct	Nitrogen, wt-pct	Sulfur wt-pct	Oxygen wt-pct	H_2 Cons., SCF/bbl	tempera-ture, °C	feed rate, LHSV
(Feed)	1.003	8.42	1.057	.25	3.29	-	-	-
1	0.921	10.81	0.352	.01	.59	1,930	325	0.50
2	.948	10.06	.631	.02	1.65	1,270	325	1.0
3	.902	11.54	.033	.01	.17	2,670	350	0.50
4	.953	9.80	.700	.02	1.58	970	310	0.50
5	.887	12.24	.001	.01	.09	2,880	375	0.50
6	.877	12.39	.001	.01	.03	3,250	400	0.50
7	.868	12.82	.001	.01	.06	5,010	400	0.35
8	.962	9.68	.742	.01	2.00	980	325	1.0

Period 4 was a test of a very mild condition after a weekend shutdown. Period 7 was a test of the liquid feed pump at a low rate. Period 8 was a brief test for decline in activity from period 2, although the entire operation was too short for significant life testing. Periods in the order of 2,1,3,5, and 6 were intended to cover the desired range of increasing upgrading.

The liquid feed and products were screened for chemical mutagens by use of the Ames assay (1,2).

Results and Discussion

The results in table 1 show the expected trends as hydrotreating severity was increased with reaction temperatures in the range of 310 to 400° C. Specific gravity of the product liquid at 375°C decreased from 1.00 for the feed to 0.89 while nitrogen decreased from 1.06 wt-pct to less than .001 wt-pct and oxygen decreased from 3.29 wt-pct to 0.09 wt-pct. Hydrogen content increased from 8.42 wt-pct in the liquid feed to 12.24 wt-pct over this same range of nitrogen removal. Calculated

hydrogen consumptions for this range of conditions varied from 970 to 2,880 SCF/bbl which is within the ranges reported by others (2,3). Precise hydrogen content of the liquid product, used in calculation of hydrogen consumption, was determined by NMR through the courtesy of Phillips Petroleum Company. Analysis of the effluent gas did not include hydrocarbons heavier than ethane. Contributions of the heavier hydrocarbons to hydrogen consumption are small for hydrotreating at conditions which cause very little cracking of hydrocarbons since most of the consumed hydrogen goes into the liquid product.

The distillation range of the liquid products was shifted downward as hydrotreating severity was increased (table 2). The magnitude of the shift of the simulated distillation is shown in the last column which indicates 8 to 22 percent of the feed is converted to material boiling below the five percent point of the feed.

TABLE 2. - Simulated distillation of liquid feed and products

Sample Period	Temp., °C., at wt-percent distilled			wt-percent converted to below 185° C
	5	50	95	
(Feed)	185	255	379	-
4	112	239	361	15
2	131	247	369	9
3	101	235	344	18
4	133	248	375	8
5	96	229	331	21
6	98	225	329	22
7	94	221	326	21
8	156	252	379	7

The increase in product material boiling below 185° C results largely from saturation of aromatic rings and olefins and from removal of heteroatoms. Some hydrocarbons boiling lower than the feed would be formed by cleaving of heteroatom linkages, with very little cracking of hydrocarbons expected. For example, all product liquids had initial boiling points close to that of benzene/cyclohexane.

The results of the Salmonella/Typhimurium Mutagenicity (Ames) assay for the feed and liquid products are given in table 3. The assay was run essentially as described by Ames(1). The assay employs specially constructed strains of Salmonella Typhimurium which are reverted by a wide variety of mutagens from requiring histidine in their growth media back to bacteria capable of synthesizing histidine.

TABLE 3. - Results of the Ames assay

Sample	Concentration, ug/plate	Number of Revertants Without/With Metabolic Activation TA 98	TA 100
Feed	250	30/1822	144/322
Feed	100	34/1122	163/348
Feed	50	27/547	150/306
Feed	25	21/316	150/204
Feed	5	31/113	134/178
Background	0	21/60	144/142
8	100	15/131	134/257
4	100	19/111	176/232
2	100	23/178	151/226
1	100	16/64	158/218
3	100	10/40	161/194
5	100	22/64	162/194
6	100	19/70	128/186
7	100	17/65	153/218
Background	0	25/66	169/220

Some chemicals require metabolic activation (addition of microsomal enzymes) prior to showing mutagenic activity; thus, data are given as number of revertants without/with metabolic activation. The Ames test has thus far demonstrated a strong correlation between positive carcinogenesis in animal tests and mutagenicity in the Ames test (1,4). However, positive results from the Ames test do not conclusively show human risk.

The untreated SRC-II was tested at five concentrations with Salmonella strains TA 98 and TA 100, generally considered the most sensitive strains. In the results indicated in Table 3, an increase in the number of revertants greater than two times the background (no SRC-II feed or product) is sometimes considered to indicate a definite positive (mutagenic) response. The plates which showed a positive response by this criteria are underlined.

Activity decreased with decreasing concentration for the untreated feed but was still nearly double the activity of the background at a concentration of 5 ug per plate. A product dose of one hundred micrograms was selected as a satisfactory screening test since a strong response was observed for the untreated SRC-II at this concentration and since no appreciable cytotoxicity was noted. The hydrogenation periods are listed in order of increasing severity of processing. Activity was decreased essentially to the background level when nitrogen content was decreased to

0.35 wt-pct, oxygen content was decreased to 0.59 wt-pct and hydrogen content was increased from 8.4 to 10.8 wt-pct. This occurred at process conditions of 325° C and 0.5 LHSV feed rate, which had been planned as the lowest reaction temperature expected to give substantial upgrading.

A more complete investigation will require testing of fractions of the coal liquid to identify more active components. Nitrogen and oxygen compounds and aromatic ring structures are important in this respect, with mutagenically active components likely to be in higher-boiling fractions. Tests on mammalian systems are also needed before making assessments concerning potential human risk.

Summary

Distillate coal liquid from the SRC-II process was hydrotreated in a bench-scale process unit to provide a range of mildly upgraded products for compositional characterization and screening for mutagenicity. Hydrogen content of the liquid was increased from 8.4 to 12.24 wt-pct over the range of process conditions which removed essentially 100 percent of the nitrogen and 95 percent of the oxygen. Results of the Ames assay indicated mutagenic activity of the liquid product decreased by an order of magnitude for 35 percent removal of nitrogen and 52 percent removal of oxygen. Liquid product with 67 percent nitrogen removal and 82 percent oxygen removal showed no mutagenic activity distinguishable from that of the background samples. The full range of effect in decreasing mutagenic activity by the Ames assay was covered by relatively mild hydrotreatment, but assessment of potential human risk must be confirmed using additional mammalian tests.

References

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